



**Bench-Scale Treatability Report in Support of a ZVI Application
in a Reactive Vessel for Treatment of cVOCs
at a Site in Zionsville, IN**

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TABLE OF CONTENTS

1.0 INTRODUCTION AND BACKGROUND	1
1.1 Background Information on the ZVI Technology	1
1.2 Approach to Technology Implementation at the Site	1
1.3 Bench-Scale Test Report Organization.....	2
2.0 BENCH-SCALE TEST OBJECTIVES AND METHODS.....	3
2.1 Bench-Scale Test Objectives.....	3
2.2 Bench-Scale Test Methods.....	3
2.2.1 Groundwater Shipment and Storage	4
2.2.2 Sampling and Analysis.....	4
2.3 Analytical Methods	5
2.3.1 Organic Analyses.....	5
2.3.2 Inorganic Analyses	6
3.1 Degradation of Volatile Organic Compounds.....	7
3.2 Determination of cVOC Degradation Parameters	8
3.3 Inorganic Results	10
4.0 FIELD-SCALE TREATMENT SYSTEM DESIGN CONSIDERATIONS	12
4.1 Rate of Passivation and Sizing of Sacrificial Zone	12
4.2 Required Residence Time for cVOCs	13
4.3 Incorporation of a Chemical Pre-treatment Zone into the Design.....	14
5.0 SUMMARY	15
6.0 REFERENCES.....	16

LIST OF TABLES

Table 1:	Iron and column properties
Table 2:	Initial cVOC composition in site water provided for the test
Table 3:	CVOC concentrations targeted in the spiked site water used in the test
Table 4:	Method Detection Limits (MDL) and Reported Detection Limits (RDL)
Table 5:	Bench-Scale Test Half-Life Values for 100% ZVI at the End of the Test (22°C).
Table 6:	Major Influent and Effluent Inorganic Chemistry.
Table 7:	30%ZVI Passivation Calculation based on Column Test Results.
Table 8:	30%ZVI Longevity Calculation based on Column Test Results.
Table 9:	Residence time calculation for the ZVI main reactor zone (100% ZVI Connelly).
Table 10:	Example Design Calculations for Connelly ZVI. Based on Residence Time Requirements in a ZVI Zone Un-affected by Passivation.

LIST OF FIGURES

Figure 1:	Schematic of the apparatus the column test set-up
Figure 2:	Photograph of the ZVI column
Figure 3:	TCE and cDCE concentration profiles versus residence time in the column with increasing pore volumes (PVs) of water passed. Broken line indicates the extent of the 30%ZVI-70%sand zone vs. the main 100% ZVI zone.
Figure 4:	VC and 111TCA concentration profiles versus residence time in the column with increasing pore volumes (PVs) of water passed. Broken line indicates the extent of the 30%ZVI-70%sand zone vs. the main 100% ZVI zone. The 30%ZVI column was replaced after 28 PVs.
Figure 5:	CVOC “breakthrough” in the influent part of the column system; including 5 cm long 30%ZVI-sand column and a 15 cm section of the 100%ZVI column. The 30%ZVI column was replaced after 28 PVs.
Figure 6:	Redox potential (Eh) and pH profiles versus residence time in the column with increasing pore volumes (PVs) of water passed. Broken line indicates the extent of the 30%ZVI-70%sand zone vs. the main 100% ZVI zone. The 30%ZVI column was replaced after 28 PVs.
Figure 7:	Eh and pH “breakthrough” in the influent part of the column system; including 5 cm long 30%ZVI-sand column and a 15 cm section of the 100% ZVI column. The 30%ZVI column was replaced after 28 PVs.

LIST OF APPENDICES

Appendix A:	Laboratory Organic Analyses for Bench-Scale Testing Involving the ZVI Technology
Appendix B:	Laboratory Inorganic Analyses for Bench-Scale Testing Involving the ZVI Technology
Appendix C:	Methodology for Headspace SPME GC/ECD determination of VOCs in water samples SPME Protocol

1.0 INTRODUCTION AND BACKGROUND

This bench-scale treatability report was prepared for ENVIRON to support the design of a granular zero valent iron (ZVI) reactive vessel for treatment of dissolved chlorinated volatile organic compounds (cVOCs) present in groundwater at a site Zionsville, IN (the “site”). The column treatability study was conducted in Adventus’ laboratory near Toronto, Ontario, Canada.

1.1 Background Information on the ZVI Technology

Numerous ZVI-based treatment systems have been successfully implemented for groundwater remediation (RTDF 2004; O’Hannesin and Gillham, 1998). The most advanced stage of application has been achieved with systems using ZVI to degrade chlorinated organic compounds. Under highly reducing conditions and in the presence of metallic surfaces, certain dissolved chlorinated organic compounds in groundwater degrade to non-toxic products such as ethene, ethane and chloride (Gillham and O’Hannesin, 1994). The process is abiotic reductive dehalogenation, with the metal serving to lower the solution redox potential (Eh) and as the electron source in the reaction. Using ZVI as the reactive metal, reaction half-lives (the time required to degrade one half of the original contaminant mass) are commonly several orders of magnitude lower than those measured under natural conditions. The technology is particularly attractive for the remediation of contaminated groundwater because of the high rates of degradation, the ZVI is relatively inexpensive, the process requires no external energy supply and because most compounds are degraded with production of few, if any, hazardous (chlorinated) organic by-products.

1.2 Approach to Technology Implementation at the Site

A ZVI reactive vessel has been proposed as a treatment technology to degrade the trichloroethene (TCE), cis 1,2-dichloroethene (cDCE), trans 1,2-dichloroethene (tDCE), vinyl chloride (VC), 1,1-dichloroethane (11DCA) and 1,1,1-trichloroethane (111TCA) present in the groundwater at the site. When viewed in the context of previous successful applications, the site appears quite amenable to treatment using this technology:

- i) all cVOCs present in the site groundwater have been successfully treated in numerous laboratory studies and field applications; and
- ii) the main inorganic constituents of the plume appeared to pose no significant impediment to technology application.

Several design parameters need to be addressed and quantified in order to apply the ZVI technology in the field. This bench-scale test was initiated to provide design parameters (cVOC degradation rates) for the anticipated maximum concentrations entering the reactive vessel. Specifically, the following factors need to be investigated to facilitate field implementation of a treatment system at the site:

- i) The degradation rates of cVOC present in the site groundwater. These rates allow the calculation of the iron thickness required to achieve cVOC concentrations below the regulatory limits.
- ii) The production and subsequent degradation rates of chlorinated compounds produced from the cVOCs originally present in the site groundwater [e.g., vinyl chloride (VC)]. These can also affect the dimensions of the treatment system.
- iii) The amount of iron material required. This amount is based on the concentrations of cVOCs present in groundwater entering the treatment zone and potential breakdown products, degradation rates and groundwater flow rate.
- iv) The effects of the process on the inorganic chemistry of the groundwater, in particular, the potential for mineral precipitation. Mineral precipitates could affect the long-term maintenance requirements of the treatment system.

1.3 Bench-Scale Test Report Organization

The remainder of this report is organized as follows:

- Section 2.0 presents the detailed objectives and methods for the bench-scale test.
- Section 3.0 presents the organic and inorganic results from the bench-scale test.
- Section 4.0 discusses the calculated residence time required for cVOC treatment to meet the target levels and provide a preliminary conceptual design for the treatment system.
- Section 5.0 summarizes the results.

2.0 BENCH-SCALE TEST OBJECTIVES AND METHODS

2.1 Bench-Scale Test Objectives

The primary objective of the bench-scale test was to provide the data necessary to determine the residence time in ZVI to degrade the cVOCs present at the site, and their chlorinated breakdown products, to below the regulatory criteria. Additionally, maintenance requirements for efficient operation of the proposed reactive vessel were evaluated. Samples collected during the laboratory column test were used to evaluate the following specific objectives:

- determine degradation rates of cVOCs using groundwater from the site;
- characterize chlorinated breakdown products, and evaluate the rates of degradation of these products; and
- evaluate changes in inorganic geochemistry as a result of the pH, Eh and alkalinity changes, including possible mineral precipitation.
- quantify the maintenance requirement for a sacrificial ZVI-sand zone proposed as part of the reactive vessel design.

2.2 Bench-Scale Test Methods

The bench-scale testing included a column apparatus containing ZVI obtained from Connelly GPM of Chicago, IL (CC-1004, 0.25 to 2.0 mm) tested using the site groundwater. To simulate the operation of the proposed above ground ZVI reactor containing a sacrificial ZVI-sand zone, the column apparatus is composed of (**Figures 1 and 2**):

- An initial column 5 cm in length packed with 30%wt ZVI and 70%wt sand; and
- A downgradient column 50 cm in length packed with 100% ZVI.

A hydraulic conductivity of 5×10^{-2} cm/sec (142 ft/day) was obtained for Connelly ZVI using a falling head permeameter test (**Table 1**). The specific surface area of the ZVI was 1.4 m²/g, which was determined by the BET method (Brunauer et al., 1938) on a Micromeretic Gemini 2375 surface analyzer.

The columns were constructed of Plexiglas™ with lengths of 0.16 ft (5 cm) for the sacrificial column and 1.64 ft (50 cm) for the main column and an internal diameter of 1.5 in (3.8 cm) (**Figures 1 and 2**). The sacrificial column was sampled from the influent and the effluent end. The main column sampling ports were positioned along the length at distances of 0.08, 0.16, 0.33, 0.50, 0.66, 1.0, and 1.3 ft (2.5, 5, 10, 15, 20, 30, and 40 cm) from the inlet end. The main column also allowed for the collection of samples from the influent (0 ft, 0 cm) and effluent lines (1.6 ft, 50 cm). Each sampling port consisted of a nylon Swagelok fitting (0.063

in, 0.16 cm) tapped into the side of the column, with a syringe needle (16G) secured by the fitting. Glass wool was placed in the needle to exclude the iron particles. The sampling ports allowed samples to be collected along the central axis of the column. Each sample port was fitted with a Luer-Lok™ fitting, such that a glass syringe could be attached to the port to collect a sample. When not in operation the ports were sealed by Luer-Lok™ plugs.

The ZVI, as received from the vendor, was packed in the main column. The sacrificial column was packed with ZVI material mixed with Ottawa sand (20-30 US mesh) at a mass ratio of 30% ZVI to 70% sand. To assure a homogeneous mixture, aliquots of iron were packed vertically in lift sections within the columns. Values of bulk density, porosity, and pore volume (PV) were determined by weight (**Table 1**). The column experiment was performed at a temperature of approximately 22°C. A low flow Masterflex™ peristaltic pump was used to feed the site water from a collapsible Teflon® bag to the influent end of the sacrificial column. The effluent line of the sacrificial column was connected to the influent end of the main column. The pump tubing consisted of Viton®, and all the other tubing was Teflon® [0.125 in (0.32 cm) OD × 0.063 in (0.16 cm) ID]. The flow velocity in the main column was about 1.6 ft/day (50 cm/day).

2.2.1 Groundwater Shipment and Storage

The groundwater samples provided by ENVIRON were collected from multiple sampling points. The bulk sample represented approximately 15% Trench 1, 15% Trench 2, 15% Trench 3, and 55% PRGS Manhole. The initial concentrations of cVOCs detected in the groundwater samples after arrival in the laboratory and homogenization are shown in **Table 2**. In consultation with ENVIRON, the site water was spiked using laboratory grade compounds to achieve a more representative cVOC composition in the water used in the test (**Table 3**).

The site water was stored at 4°C until required at which time it was siphoned from the field sample bottles into collapsible Teflon® bag. As noted in **Appendix A** by reservoir number [RN], the influent reservoir was filled two times [a-b] over the course of the test.

2.2.2 Sampling and Analysis

The column system was sampled for cVOCs every 6 to 7 PVs for 40 pore volumes of flow, resulting in a total of 6 complete cVOC column profiles. After removing the stagnant water from the sampling needle, 4.0 mL samples were collected from the sampling ports using glass on glass syringes, transferred to glass sample bottles, and analyzed immediately (no

holding time). Samples for organic analyses, redox potential (Eh), pH, nitrate, chloride and sulphate were collected from each port as well as from the influent solution and the effluent overflow bottles (**Appendix A**).

Additional samples for complete inorganic analyses (**Appendix B**) were obtained from the influent solution and the effluent overflow bottles towards the end of the test.

2.3 Analytical Methods

2.3.1 Organic Analyses

The less volatile halogenated organics such as tetrachloroethene (PCE), trichloroethene (TCE) and 1,1,1-trichloroethane (111TCA) were extracted from the water sample within the glass sample bottle using pentane with an internal standard of 1,2-dibromoethane, at a water to pentane ratio of 2.0 to 2.0 mL. The sample bottles are placed on a rotary shaker for 15 minutes to allow equilibration between the water and the pentane phases, then the pentane phase is transferred to an autosampler bottle. Using an Agilent 7683 autosampler, a 1.0 μ L aliquot of pentane with internal standard was automatically injected directly into a Agilent 6890N gas chromatograph. The chromatograph was equipped with a Ni^{63} electron capture detector (ECD) and DB-624 megabore capillary column (30 m x 0.538 mm ID, film thickness 3 μ m). The gas chromatograph had an initial temperature of 40°C, with a temperature time program of 10°C/minute reaching a final temperature of 150°C. The detector temperature was 300°C. The carrier gas was helium and makeup gas was 5% methane and 95% argon, with a flow rate of 30 mL/min.

For the more volatile compounds such as cis 1,2-dichloroethene (cDCE), trans 1,2-dichloroethene (tDCE), 1,1-dichloroethene (11DCE) and vinyl chloride (VC), 4.0 mL samples were collected in glass on glass syringes and placed in 10 mL Telfon[®] faced speta crimp cap vials, creating a headspace with a ratio of 6.0 mL headspace to 4.0 mL aqueous sample. The samples are placed on a rotary shaker for 15 minutes to allow equilibration between the water and gas phase. Using an Agilent G1888 headspace auto sampler, a 1 mL stainless steel sample loop injects the samples directly onto an Agilent 6890N gas chromatograph. The chromatograph was equipped with a HNU photoionization detector (PID) with a bulb ionization potential of 10.2 eV. The gas chromatograph was fitted with a fused silica capillary NSW-PLOT column (15 m x 0.53 mm ID). The samples are placed in the analyzer oven for 2 minutes at 75°C, and subsequently injected onto the gas chromatograph. The temperature program was initially set at 50°C, then increased at 20°C/min to 200°C and held for 7 minutes. The injector and detector temperatures are 200°C and 150°C, respectively. The

carrier gas is helium with a flow rate of 14 mL/min. Data is collected with a HP Pentium XP computer using GC-Chemstation Version B.01.03.

Analytical methods used for detection of 11DCA are described in **Appendix C**.

Method detection limits (MDL) were determined for each compound as the minimum concentration of a substance that can be identified, measured and reported with 99% confidence that the analyte concentration is greater than zero. The MDLs were determined from analysis of samples from a solution matrix containing the analytes of interest. Although MDLs are reported, these values are not subtracted from any reported cVOC concentrations (**Appendix A**). The reason for this is that it indicates that the organic concentrations are approaching or advancing within the column, and is helpful when determining degradation rates. Detection limits for all compounds, as given in **Table 4**, were determined using the EPA procedure for MDL (US EPA, 1982).

2.3.2 Inorganic Analyses

Eh was determined using a combination Ag/AgCl reference electrode with a platinum button and an Oakton™ Model meter. The electrode was standardized with an ORP standard (ThermElectron Corporation). Millivolt (mV) readings were converted to Eh, using the electrode reading and the standard potential of the Ag/AgCl electrode at a given temperature. The pH measurements were made using a combination pH/reference electrode and an Oakton™ Model meter, standardized with the pH buffer 7 and the appropriate buffer of either 4 or 10. A 2.0 mL sample was collected with a glass on glass syringe and analyzed immediately for Eh and then pH.

Two complete column profiles were collected from each column for nitrate (as N), sulphate and chloride by collecting a 5 mL sample in glass vials (**Appendix A**). These samples were sent to SGS Canada Inc. for analysis using ion chromatography. At the end of the test, two water samples were collected from the influent and effluent of each column and sent to Maxxam Analytics Inc. for cation and anion analyses. Cation analyses, included Fe, Na, Mg, Ca, K, Mn, etc. were performed using inductively coupled plasma (ICP). All cation samples were unfiltered and acidified to a pH of 2 with nitric acid. Anion analyses, including Cl, NO₃, SO₄, etc. were performed using ion chromatography. In addition, alkalinity, ammonia (as N), total organic carbon (TOC) and dissolved organic carbon (DOC) analyses are determined by colorimetry and were sampled from the column influent and effluent. The TOC and DOC samples were unfiltered and acidified to a pH of 2 with sulphuric acid. Detection limits for the inorganic parameters are included in **Table 4**.

3.0 BENCH-SCALE TEST RESULTS

3.1 Degradation of Volatile Organic Compounds

Samples for measurement of cVOC concentrations along the length of the column were taken approximately every 6 to 7 PVs (**Appendix A**). Using the distance for each sampling port and flow velocity, the residence time was calculated for each port. The results were plotted as cVOC concentration ($\mu\text{g/L}$) versus residence time within the column (hrs). At a flow velocity of about 1.6 ft/day, one pore volume corresponded to a residence time of about 27 hrs in the column system (sacrificial + main column) (**Table 1**). A total of about 40 PVs of water were passed through the system.

Major cVOC degradation profiles collected are shown in **Figures 3** and **4**. The first sampling point at 1.7 hr residence time represents the effluent of the 30% ZVI-sand zone. For all cVOC measured, results at that point showed a significant removal of those compounds, with a noticeable gradual breakthrough with time (**Figure 5**). The diminishing reactivity in the 30% ZVI zone coincided with a decreasing capacity to create reducing conditions (**Figures 6 and 7**). Those passivation trends were anticipated since the function of the sacrificial zone was to “pre-treat” the water flowing into the main reactor and the zone was designed to be changed periodically. In the test, the sacrificial column was changed after about 28 PVs of flow (after the 4th cVOC profile). However, the temporal cVOC trends in the main column indicated a significant degree of passivation in the influent part of the 100% ZVI column occurred before the change out (**Figure 5**).

The cVOC concentration profiles in the main 100% ZVI column showed TCE, cDCE, VC and 111TCA degradation to non-detectable levels within a residence time of 7.6 hrs or less at the end of the test (**Figures 3 to 5**). The higher chlorinated compounds, 111TCA and TCE were removed faster than the lower chlorinated compounds, cDCE and VC, consistent with typical ZVI degradation trends. The lower chlorinated compounds were also much more sensitive to the passivation effects. The obtained cVOC data were used to calculate the degradation rates, as described in Section 3.2.

Three profiles of 11DCA were collected and showed considerable variability among the sampling events (**Appendix A**). In general the maximum influent concentration of about 100 $\mu\text{g/L}$ increased to a maximum of 240 $\mu\text{g/L}$ as an effect of partial dechlorination pathway of 111TCA, but non-detectable values were measured in the effluent part of the 100% column. The reported site remediation goal for 11DCA is 990 $\mu\text{g/L}$; therefore we did not consider it as a contaminant of concern.

3.2 Determination of cVOC Degradation Parameters

The cVOC degradation trends observed in groundwater in contact with ZVI are typically described using first-order kinetics:

$$C = C_o e^{-kt} \quad (1)$$

or

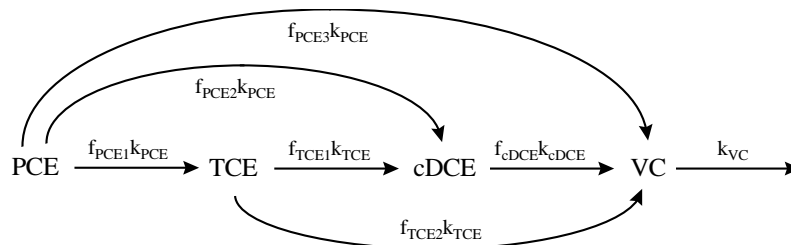
$$\ln\left(\frac{C}{C_o}\right) = -kt \quad (2)$$

where: C = cVOC concentration in solution at time t,
 C_o = cVOC concentration of the influent solution,
 k = first-order rate constant, and
 t = time.

The time at which the initial concentration declines by one-half, ($C/C_o = 0.5$), is the half-life.

ETI has developed a first-order kinetic model to simulate the degradation of cVOCs with ZVI. In the model, potential breakdown products are concurrently produced and degraded as described by first-order kinetic equations. The model is an expression of the chemistry that is observed in the solution phase. For example, for the chlorinated ethenes (PCE, TCE, cDCE and VC) the production of chlorinated acetylene via a β -elimination pathway is considered to be the dominant degradation pathway (Eykholt, 1998; Arnold and Roberts, 1999). However, since chlorinated acetylenes are unstable, short-lived, intermediates that are rapidly reduced to ethene (Roberts et al., 1996; Sivavec et al., 1997), these compounds are not typically detected in the solution phase and are therefore not explicitly contained in the degradation model.

The equations contained in the model were developed by ETI to describe the first-order kinetic degradation process occurring in a ZVI groundwater treatment zone. For example, PCE, TCE, cDCE and VC the model takes the form:



where: f = mole fraction (or percent molar conversions)
 k = first-order rate constant

In order to determine the cVOC concentrations at a given time the following first-order equations are used:

$$dPCE / dt = -k_{PCE}PCE \quad (3)$$

$$dTCE / dt = f_{PCE1}k_{PCE}PCE - k_{TCE}TCE \quad (4)$$

$$dcDCE / dt = f_{PCE2}k_{PCE}PCE + f_{TCE1}k_{TCE}TCE - k_{cDCE}cDCE \quad (5)$$

$$dVC / dt = f_{PCE3}k_{PCE}PCE + f_{TCE2}k_{TCE}TCE + f_{cDCE}k_{cDCE}cDCE - k_{VC}VC \quad (6)$$

These equations were adapted for the computer program Scientist[®] for Windows[®] Version 2.0 (1995). The Scientist[®] program can be used to fit the first-order equations to experimental data using the least squares best-fit method. Least squares fitting is performed using a modified Powell algorithm to find a local minimum of the sum of squared deviations between observed data and model calculations. The degradation rate and molar conversion are determined for each compound sequentially starting with the most chlorinated compound.

The results from the model include half-lives for all cVOCs selected and statistical fit data including coefficient of determination (r^2) values. The r^2 values indicate how well the degradation model represents the experimental data. The half-lives determined from the cVOC profiles are shown in **Table 5**, along with the corresponding r^2 values. Degradation parameters for the last three cVOC profiles are shown in **Appendix A**.

The degradation model provided good fits to the cVOC concentration profiles with r^2 values of 0.84 or higher for the cVOCs (**Table 5**). The obtained room temperature degradation half-lives values at the end of the test were 0.54 hrs for TCE, 1.9 hrs for cDCE, 1.3 hrs for VC and 0.63 hrs for 111TCA. Note that to obtain the half-lives the concentration trends starting behind the passivation front that migrated through the sacrificial column and a part of the 100%ZVI column were used (**Appendix A**). These “unpassivated” half-lives values are considered slightly better than typical. In comparison, the average half-lives based on over 50 results from column test at room temperature for various commercial ZVIs were 1.3 hrs (SD=0.9 hrs) for TCE, 3.4 hrs (SD=2.2 hrs) for cDCE and 3.2 hrs (SD=2.9 hrs) for VC (Gillham et al., 2010).

The half-life data were used to develop residence time requirements in the 100% ZVI reactor zone in Section 4.2.

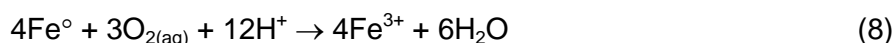
3.3 Inorganic Results

Two influent and effluent samples were collected from the columns as steady state approached (**Appendix B**). Changes in inorganic chemical constituents observed in the influent and effluent groundwater are summarized in **Table 6**. **Appendix B** contains the inorganic analytical data.

When iron is exposed to water, several reactions occur as a result of iron corrosion:



This iron corrosion drives the geochemical changes that occur as groundwater flows through the PRB. When groundwater first contacts the ZVI, any dissolved oxygen present is consumed via iron corrosion:

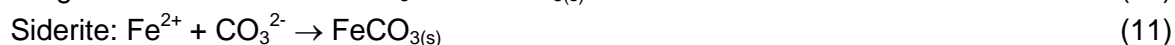
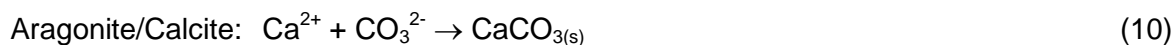


After the initial, rapid depletion of any dissolved oxygen, the water corrosion of iron dominates to produce hydrogen and hydroxide resulting in a pH increase and decline in Eh:



Figure 6 shows the redox potential (Eh) and pH profiles in the column system. The Eh decreased from an influent value of about +600 mV to below -450 mV within the column. The pH increased from influent values of about 7.0 in to about 8.7 within the column. Creation of highly reducing and alkaline conditions is the expected effect of ZVI corrosion chemistry. Both Eh and pH values fluctuated in the influent part of the column as the 30%ZVI zone was slowly being passivated (**Figure 7**).

The influent calcium concentration of 130 mg/L decreased to 44 mg/L in the effluent of the ZVI column (**Table 6**). The carbonate alkalinity value in the columns decreased from initial values of about 241 mg/L to 5 mg/L within the ZVI column. Based on the stoichiometry of calcium carbonate formation (eq. 10), the observed losses in alkalinity were higher than those expected from the formation of calcium carbonate. Therefore, iron carbonate (siderite) was likely also formed (eq. 11).



In analyses of iron obtained from previous laboratory studies and field sites, siderite (FeCO_3) as well as both calcite and aragonite, both forms of calcium carbonate, have been identified. Potassium and sodium behave as conservative tracers in iron systems and as expected their concentrations remained essentially unchanged within the columns (**Table 6**). A significant increase in chloride concentration due to the dissolved chloride created by the cVOC dechlorination was not expected considering relatively low influent cVOC concentrations in the columns. Decreases in concentrations of silicon observed in the columns were expected in response to geochemical conditions created by ZVI.

The influent concentrations of DOC and TOC varied from 11 to 15 mg/L, and about 4 mg/L was lost in the column system (**Table 6**). There has been a considerable amount of research into the influence of DOC on volatile organic compounds (VOCs) degradation rates with ZVI. In bench-scale testing, we have observed varying degrees of impact in water containing 10's to 100's of mg/L non-chlorinated DOC (dissolved organic carbon). Some high DOC concentrations have caused negative impacts (lower VOC degradation rates), while other high DOC water have shown no impact what so ever. Other laboratory studies (e.g., Tratnyek and Scherer, 1998; Klaussen et al., 2002; Marconetto et al., 2004; Dries et al., 2004) have investigated affects of specific humic and fulvic acids that make up DOC in groundwater. This research has shown that the impact on degradation rates is compound specific (for example, carbon tetrachloride rates may be less affected than tetrachloroethene rates in a given groundwater), and also dependent on the composition and levels of the DOC fraction. Limitations of VOC degradation in the presence of DOC have been attributed to two processes: competition between VOCs and DOC for occupation of iron reactive sites and interactions between VOCs and DOC in solution. The migration of the passivation front in this column test was relatively fast, compared to other high carbonate water ZVI tests, therefore we believe that TOC/DOC affected the trends observed in this column tests.

The concentration of sulfate detected at 240 mg/L in the influent of the column system, remained unchanged along the column lengths within the test period. However, declines in sulfate concentrations have been observed at a number of field sites as groundwater passes through the iron treatment zones and microbial sulfate reducing activity develops with time.

These results indicate that carbonate mineral precipitation and TOC/DOC influence will affect the long-term performance of ZVI at this site, dependent on the mass fluxes. Therefore, the design and operation of a ZVI vessel at the site should include a method of mitigating this effect.

4.0 FIELD-SCALE TREATMENT SYSTEM DESIGN CONSIDERATIONS

Laboratory column data were used to obtain a ZVI design for the water tested. As per the objectives of the test, specific design parameters were obtained for determining a theoretical rate of passivation of the pre-treatment 30%ZVI-70%Sand zone and the sizing of the 100%ZVI zone in a reactive vessel application. Two processes were considered; the gradual iron-sand passivation in the 30% ZVI sacrificial zone and VOC degradation to below site standards in the main 100% ZVI zone.

4.1 Theoretical Rate of Passivation in 30%ZVI Zone

Based on the inorganic chemistry results presented in Section 3.3, precipitation of calcium carbonate within the ZVI bed, in combination with iron hydroxides, and TOC/DOC effects appeared to be responsible for the observed loss of iron reactivity in the pre-treatment zone and the main 100%ZVI column.

We have quantified the rate of passivation in the column test with respect to the temporal migration of concentration profiles of major VOC compounds as well as the gradual increases of Eh at the effluent of the 30%ZVI column over the test period (**Figures 5 and 6**). Based on the observed trends, the 50% breakthrough of cDCE occurred in the effluent of the 30%ZVI column after about 18 PVs of flow. At the same time the Eh values at this sampling point increased significantly to about 148 mV, indicating the zone had lost its capacity to remove carbonate and dissolved oxygen. Therefore, using this passivation evaluation method, a 5 cm 30%ZVI-70%Sand thickness was “passivated” after 18 PVs of flow.

We have assumed that calcium carbonate was the main mineral phase contributing to the observed loss of iron reactivity. Therefore, the passivation rate was normalized with respect to the influent level of carbonate alkalinity measured in the test. The reduction capacity of the ZVI-sand zone can be calculated by dividing the alkalinity (Alk.) [Average Alk. concentration \times pore volume \times number of pore volumes] by the mass of passivated material [Passivated column zone length \times column cross-section area \times iron bulk density]. Specific alkalinity reduction calculations are shown in **Table 7**. The obtained alkalinity reduction rate value is 14.8 mg_{Alk}/g_{Fe-sand} for the 30% Connolly ZVI-sand mix.

We have assumed that the sacrificial zone would be sized for a residence time of 0.25 days, based on previous ZVI vessel designs. Based on the passivation rate obtained in the test and assuming chemistry of the influent similar to that used in this test, this zone would need to be changed every about 2 months (**Table 8**). Due to the need of frequent change out of the sacrificial zone, other pretreatment methods to further mitigate the passivation process

should be considered, as discussed in Section 4.3. It should be noted that further mitigation of the passivation effects would prolong the life of the sacrificial zone.

4.2 Required Residence Time for cVOCs

The laboratory half-lives were obtained at a temperature of 22°C. We have assumed that the minimum field groundwater temperature in the reactor will be 5°C to 10°C. Based on previous research, cVOC degradation half-lives increase by 100% per every 5°C to 8°C temperature decrease within a temperature range of 5 to 25°C (O'Hannesin et al., 2004). Therefore, the laboratory half-life values were increased by a factor of 3 to obtain the anticipated field values (**Table 9**).

Preliminary residence time calculations for a field application were performed assuming the cVOC concentration values in the waters used for the bench scale test (**Table 9**). The Scientist® program described in Section 3.2 was used to simulate the change in cVOC concentrations over time using the first-order kinetic equations. In simulation mode, the model calculates the cVOC concentrations over time, from which the time required for the cVOCs to degrade to their regulatory criteria can be determined.

Based on those simulations, the residences time required to achieve the clean-up targets provided by ENVIRON in 100% Connelly ZVI at the site is 20 hrs, assuming the influent concentrations of cVOCs similar to those used in the column test (**Table 9**). The required amount of ZVI can be calculated from:

$$vol = \frac{Qt}{n}$$

where:

- Q = flow rate
- t = residence time
- n = porosity (0.6 for 100% iron)

Table 10 summarizes the reactor sizing calculations for the main reactive zone unaffected by mineral precipitation, assuming the effect of inorganic precipitation would be mitigated by another pretreatment method as described in Section 4.3.

4.3 Incorporation of a Chemical Pre-treatment Zone into the Design

As discussed in Section 4.1, passivation processes observed during the bench test could have a significant effect on the effective life of a ZVI reactor at the site. One option that could be considered to lower maintenance requirements in a ZVI reactor at this site is the incorporation of a calcium and alkalinity removal zone. For instance, a water softening system and/or pH adjustment could be used to treat the water before it enters the ZVI reactor. Previous research has shown that sodium and chloride that would result from this type of pre-treatment would not have a significant adverse effect on ZVI reactivity. Site-specific testing of these pretreatment methods is recommended prior to their application in order to confirm their efficacy and for design purposes. In particular, potential introduction of additional dissolved oxygen and cVOC volatilization during the pre-treatment should be evaluated. Based on previous experience, the use of a scavenging zone containing a ZVI-sand mix would still have merit (i.e.; dissolved oxygen removal) even if this type of chemical pre-treatment was applied.

5.0 SUMMARY

Bench-scale testing using groundwater from a site in Zionsville, IN showed that:

- i) Connelly ZVI degraded the cVOCs present in the site water. Degradation rates in the test were similar to those typically observed in previous tests for the same ZVI source and other groundwaters with comparable cVOC composition and concentrations.
- ii) Based on the field anticipated half-lives at field groundwater temperature and the cVOC concentrations tested, a residence time of 20 hrs would be required in a 100% Connelly ZVI zone unaffected by passivation to achieve the site clean-up target levels.
- iii) The tested site water contained relatively high concentrations of calcium, carbonate alkalinity and TOC/DOC which caused relatively fast passivation of the ZVI-sand pretreatment zone and the 100% ZVI zone in the column system.
- iv) It is imperative that the carbonate precipitate and other passivation effects be accommodated in a ZVI treatment reactor design. One option to mitigate the passivation effects is the use of a sacrificial zone prior to the main ZVI reactor. Based on the test results, use of a 30%iron/70%sand sacrificial zone alone for this purpose would require a relatively frequent change out to remain effective. An option for mitigating the observed passivation effects that could be evaluated is pre-treatment of the reactor influent water using a water softening system and/or pH adjustment used in combination with the iron-sand sacrificial zone for dissolved oxygen removal.

6.0 REFERENCES

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Table 1: Iron and Column Properties

Iron:		
Source	Connelly-GPM, Chicago, IL	
Grain Size	2.0 to 0.25 mm (-8 to +50 mesh)	
Surface Area	1.4 m ² /g	
Hydraulic Conductivity	5.0 × 10 ⁻² cm/sec (142 ft/day)	
Column:	30%ZVI-70%Sand	100%ZVI
Flow Rate	334 mL/day	
Length	5 cm	50 cm
Residence Time	1.7 hr	25.4 hr
Pore Volume	25 mL	353 mL
Total Porosity	0.44	0.62
Bulk Density	1.91 g/cm ³	2.70 g/cm ³
Iron to Volume of Solution Ratio	1.3 g : 1 mL	4.34 g : 1 mL

Table 2: Initial cVOC composition in site water provided for the test.

Sample	VC	11DCE	tDCE	cDCE	TCE	PCE	111-TCA	1,1-DCA
	(ug/L)							
Cooler 1 Bottle 1	10	0.82	5.5	175	17	1.2	43	88
Cooler 1 Bottle 2	11	0.75	5.7	173	17	1.1	44	59
Cooler 2 Bottle 1	10	0.79	5.9	198	17	1.1	45	73
Cooler 2 Bottle 2	11	0.82	5.8	180	18	1.2	47	103
Avg.=	10	0.80	5.7	181	17	nd	45	81

Table 3: cVOC concentrations targeted in the spiked site water used in the test.

Concentration (ug/L)				
TCE	cDCE	tDCE	VC	111TCA
~60	~800	~25	~80	350

Table 4: Method Detection Limits (MDL) and Reported Detection Limits (RDL)

Organic Compounds:	MDL (µg/L)
Tetrachloroethene (PCE)	0.3
Trichloroethene (TCE)	0.3
Cis 1,2-dichloroethene (cDCE)	0.7
Trans 1,2-dichloroethene (tDCE)	0.6
1,1-Dichloroethene (11DCE)	0.6
Vinyl chloride (VC)	0.9
1,1,1-Trichloroethane (111TCA)	0.35
1,1-Dichloroethane (11DCA)	10
Inorganic Compounds:	RDL (mg/L)
Barium (Ba)	0.002
Boron (B)	0.01
Calcium (Ca)	0.2
Iron (Fe)	0.1
Magnesium (Mg)	0.05
Manganese (Mn)	0.002
Potassium (K)	0.2
Silicon (Si)	0.05
Sodium (Na)	0.1
Strontium (Sr)	0.001
Chloride (Cl ⁻)	1
Nitrate (as N) (NO ₃)	0.1
Sulfate (SO ₄)	1
Alkalinity (mg CaCO ₃ /L)	1
Ammonia, Total (as N) (NH ₃ ⁺)	0.1
Dissolved Organic Carbon (DOC)	0.2
Total Organic Carbon (TOC)	0.2
Calculated Total Dissolved Solids (TDS)	1

Table 5: Bench-Scale Test Half-Life Values for 100% ZVI at the End of the Test (22°C).

Volatile Organic Compound	Influent Concentration ^a (µg/L)	Half-Life at Temperature 22°C (hr)	Coefficient of Determination (r ²)	Molar Conversion (%)	
TCE	46 (11)	0.54	1.000	--	--
cDCE	736 (223)	1.9	0.844	TCE → cDCE	0%
VC	65 (16)	1.3	0.869	cDCE → VC	9%
111TCA	324 (4)	0.63	1.000	--	--

^a Value in the system influent. Values in parentheses are the influent values in the 100%ZVI used in first-order fitting of half-lives

Table 6: Major Influent and Effluent Inorganic Chemistry.

Constituent	Sampling at 33 PVs		Sampling at 38 PVs		Units
	Feed	Effluent	Feed	Effluent	
Sulfate	240	230	240	240	mg/L
Alkalinity (Total as CaCO ₃)	263	6	241	5	mg/L
Chloride (Cl)	19	21	19	21	mg/L
Nitrate (N)	0.5	ND	0.5	ND	mg/L
Ammonia-N	ND (1)	ND (1)	ND (1)	ND (1)	mg/L
Organic Carbon	11.4	7.7	14.9	9.7	mg/L
Organic Carbon (TOC)	11	8.7	15	11	mg/L
Barium (Ba)	49	78	47	71	ug/L
Boron (B)	88	570	82	520	ug/L
Calcium (Ca)	130,000	47,000	130,000	44,000	ug/L
Iron (Fe)	ND	ND	ND	ND	ug/L
Magnesium (Mg)	41,000	34,000	42,000	34,000	ug/L
Manganese (Mn)	ND	250	ND	250	ug/L
Potassium (K)	3,200	3,400	3,300	3,300	ug/L
Silicon (Si)	5300	320	5400	140	ug/L
Sodium (Na)	20,000	21,000	21,000	21,000	ug/L
Strontium (Sr)	380	100	390	86	ug/L
Calculated TDS	631	362	609	362	mg/L

Table 7: 30%ZVI Passivation Calculation based on Column Test Results.

Influent Conc. Alkalinity (mg/L)	PV (L)	No. PVs	Alk. Mass Flux (mg)	Passivated length (cm)	Column x-sectional area (cm ²)	Material Bulk density (g/cm ³)	Passivated mass (g)	Alk. reduction capacity (mg _{Alk} /g _{Fe-sand})
250	0.353	18	1588.5	5	11.34	1.9	107.7	14.8

Table 8: 30%ZVI Longevity Calculation based on Column Test Results.

Conc. inorg. (mg/L)	Flow (gpm)	RT required (day)	Volume of reactor (ft ³)	Porosity	Mass Flux (mg Alk./yr)	Alk. reduction capacity (mg/cm ³ material)	Material volume removal capacity (mg of Alk.)	Longevity (yrs)
250	5	0.25	602	0.40	2,487,018,750	28 ^a	477,457,487	0.19
250	10	0.25	1204	0.40	4,974,037,500	28 ^a	954,914,974	0.19

^a From Table 7, using a bulk density of 1.9 g/cm³ for 30%ZVI-70%sand material from the column test

Table 9: Residence time calculation for the ZVI main reactor zone (100% ZVI Connelly).

cVOC	Anticipated Field Concentration ^a (µg/L)	Target Level ^b (µg/L)	Field Anticipated Half-Life ^c (hrs)	Field Residence Time ^d (hr)
TCE	60	10	1.6	20
cDCE	800	70	5.7	
VC	80	10	3.3	
111TCA	350	200	1.9	

^a Targeted spike concentrations in waters used in the column test

^b Provided by ENVIRON

^c Laboratory half-lives obtained at the end of test and corrected by a factor of 3 to a minimum expected field temperature of 5 to 10°C

^d Conservative value, not accounting for the partial degradation in the sacrificial zone

Table 10: Example Design Calculations for Connelly ZVI. Based on Residence Time Requirements in a ZVI Zone Un-affected by Passivation.

Parameter	100% ZVI zone
Q=5 gpm	
Residence time (hrs)	20
Material volume (ft ³)	1,337 ^a
Bulk density (ton/ft ³)	0.075 ^b
ZVI amount (ton)	100
Q=10 gpm	
Residence time (hrs)	20
Material volume (ft ³)	2,674 ^a
Bulk density (ton/ft ³)	0.075 ^b
ZVI amount (ton)	201

^a Porosity of 0.60 assumed 100% ZVI

^b Bulk density of Connelly iron reported by manufacturer

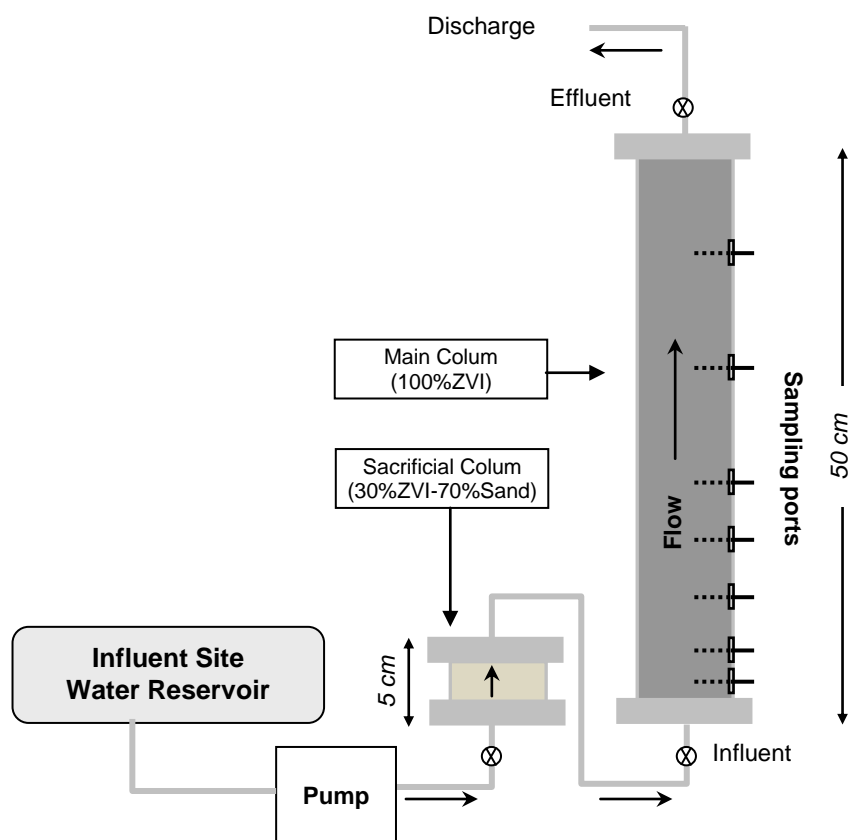


Figure 1: Schematic of Column Test Setup.

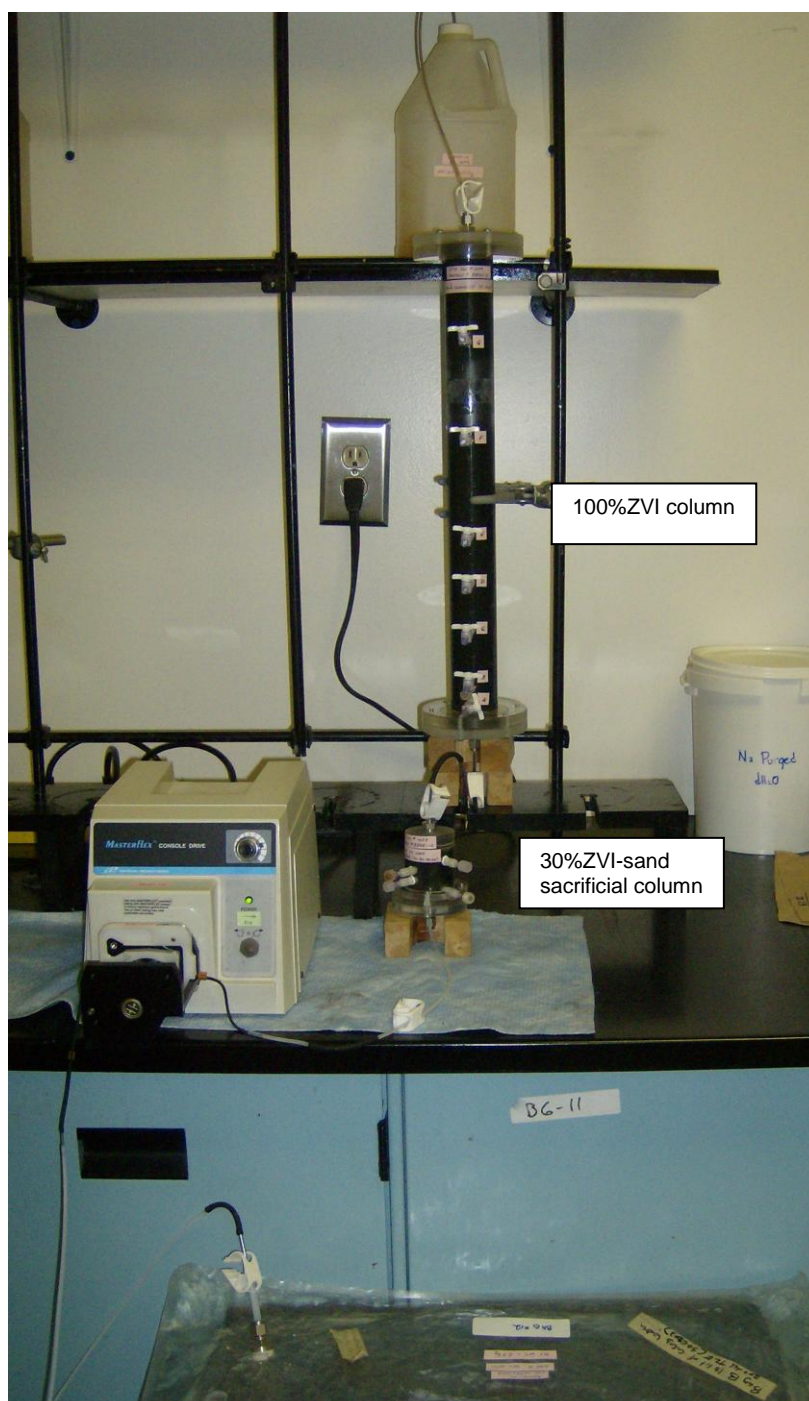


Figure 2: Photograph of ZVI columns.

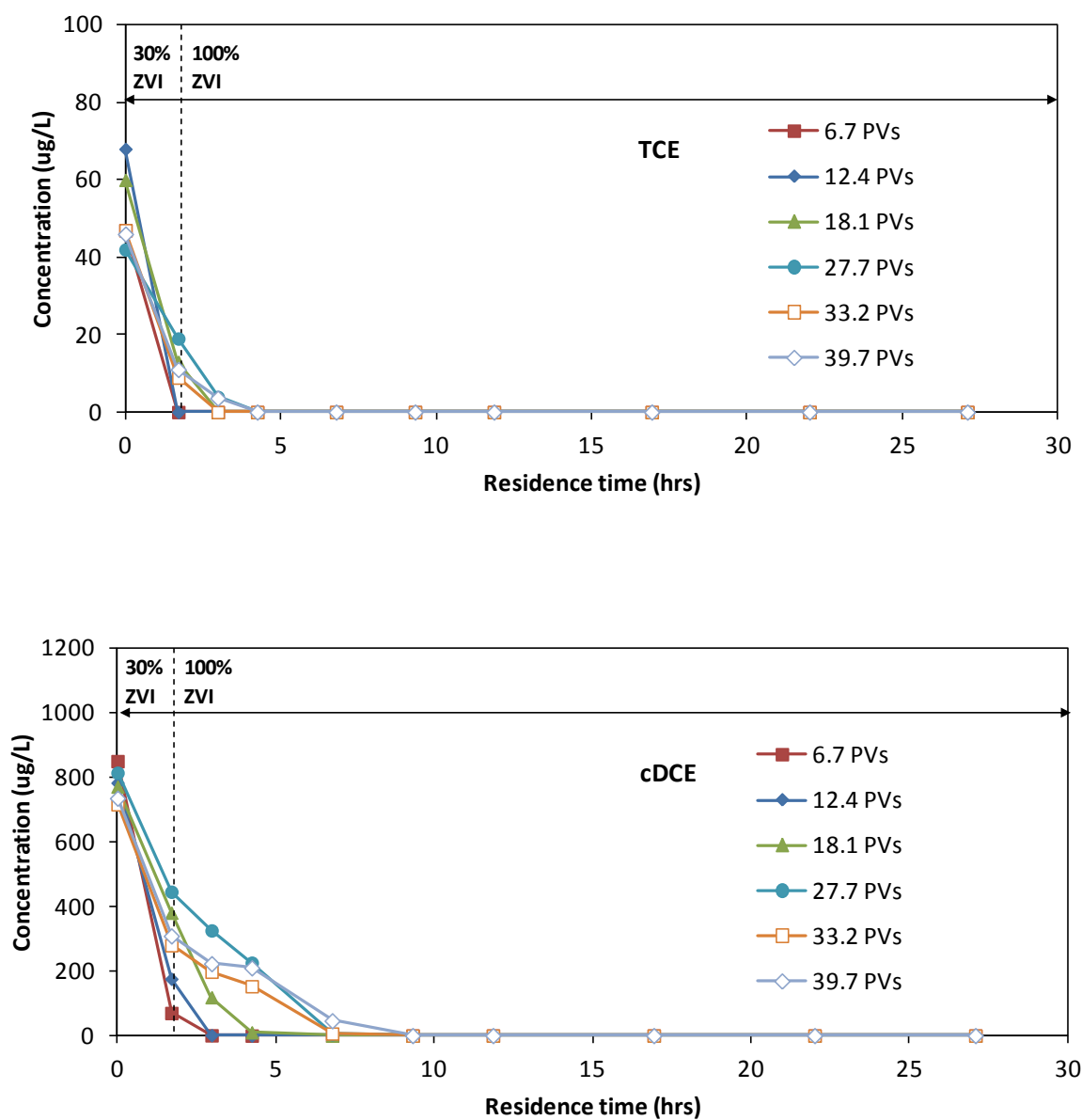


Figure 3: TCE and cDCE concentration profiles versus residence time in the column with increasing pore volumes (PVs) of water passed. Broken line indicates the extent of the 30% ZVI-70% sand zone vs. the main 100% ZVI zone.

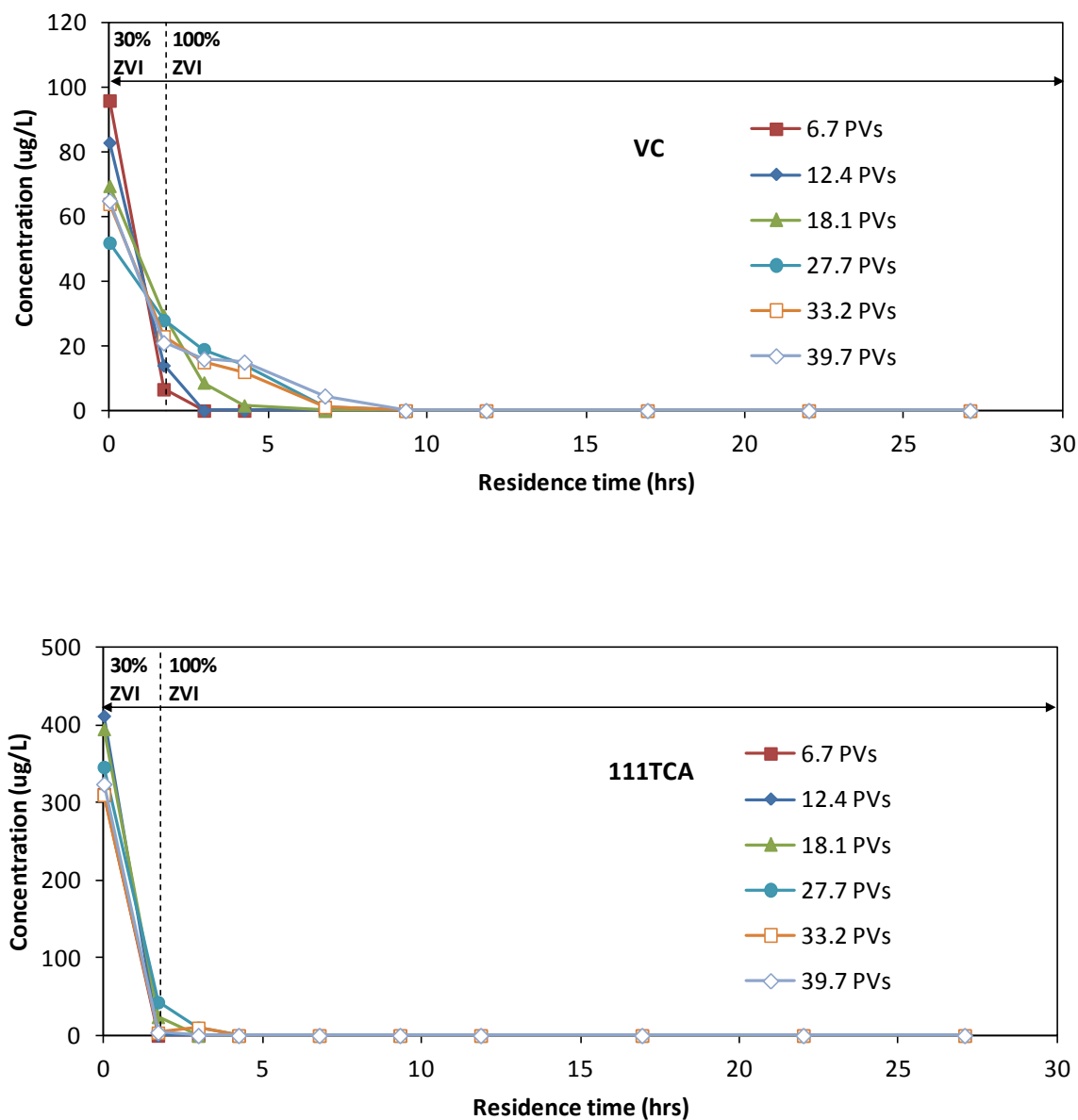


Figure 4: VC and 111TCA concentration profiles versus residence time in the column with increasing pore volumes (PVs) of water passed. Broken line indicates the extent of the 30% ZVI-70% sand zone vs. the main 100% ZVI zone. The 30%ZVI column was replaced after 28 PVs.

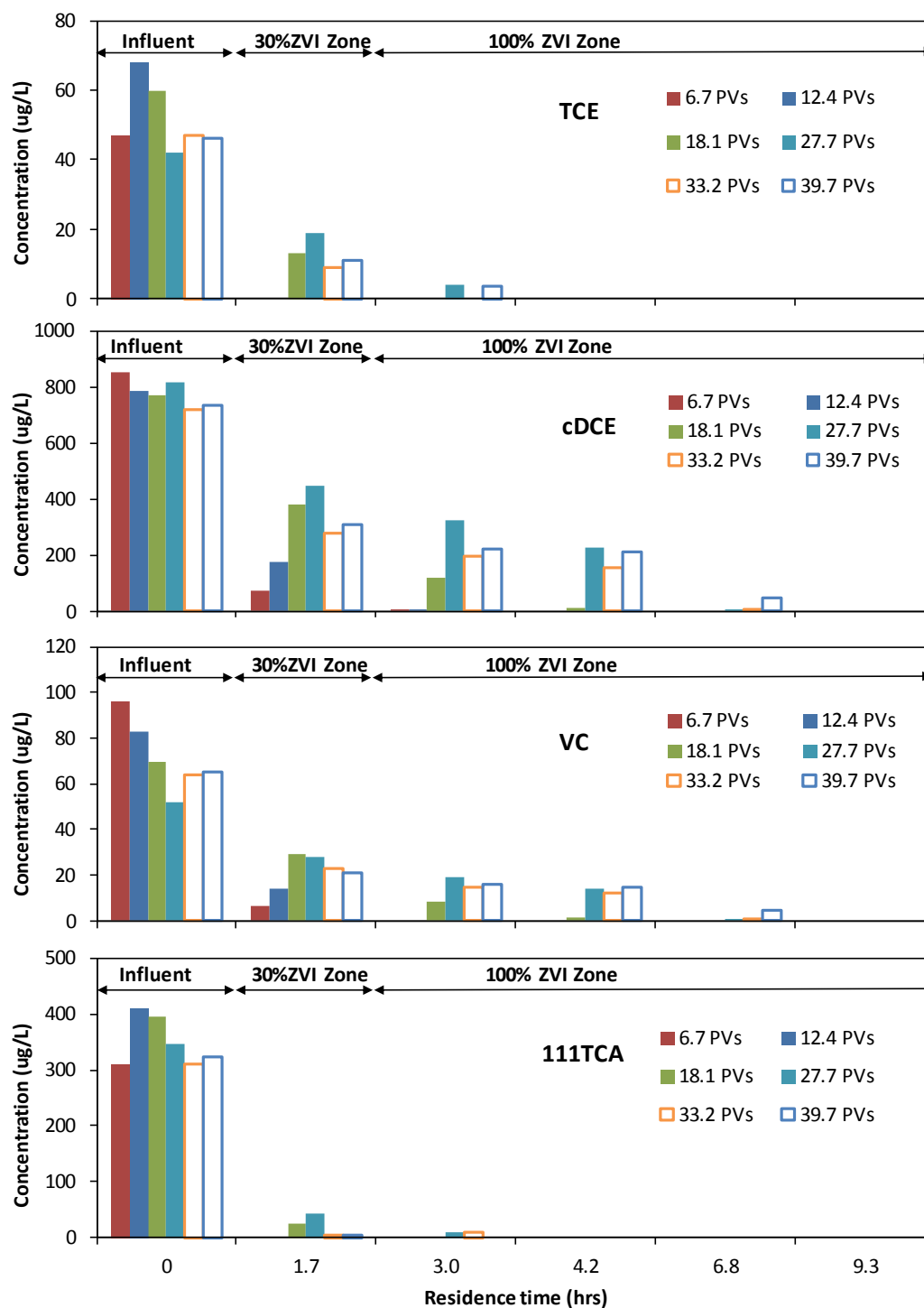


Figure 5: CVOC “breakthrough” in the influent part of the column system; including 5 cm long 30%ZVI-sand column and a 15 cm section of the 100% ZVI column. The 30%ZVI column was replaced after 28 PVs.

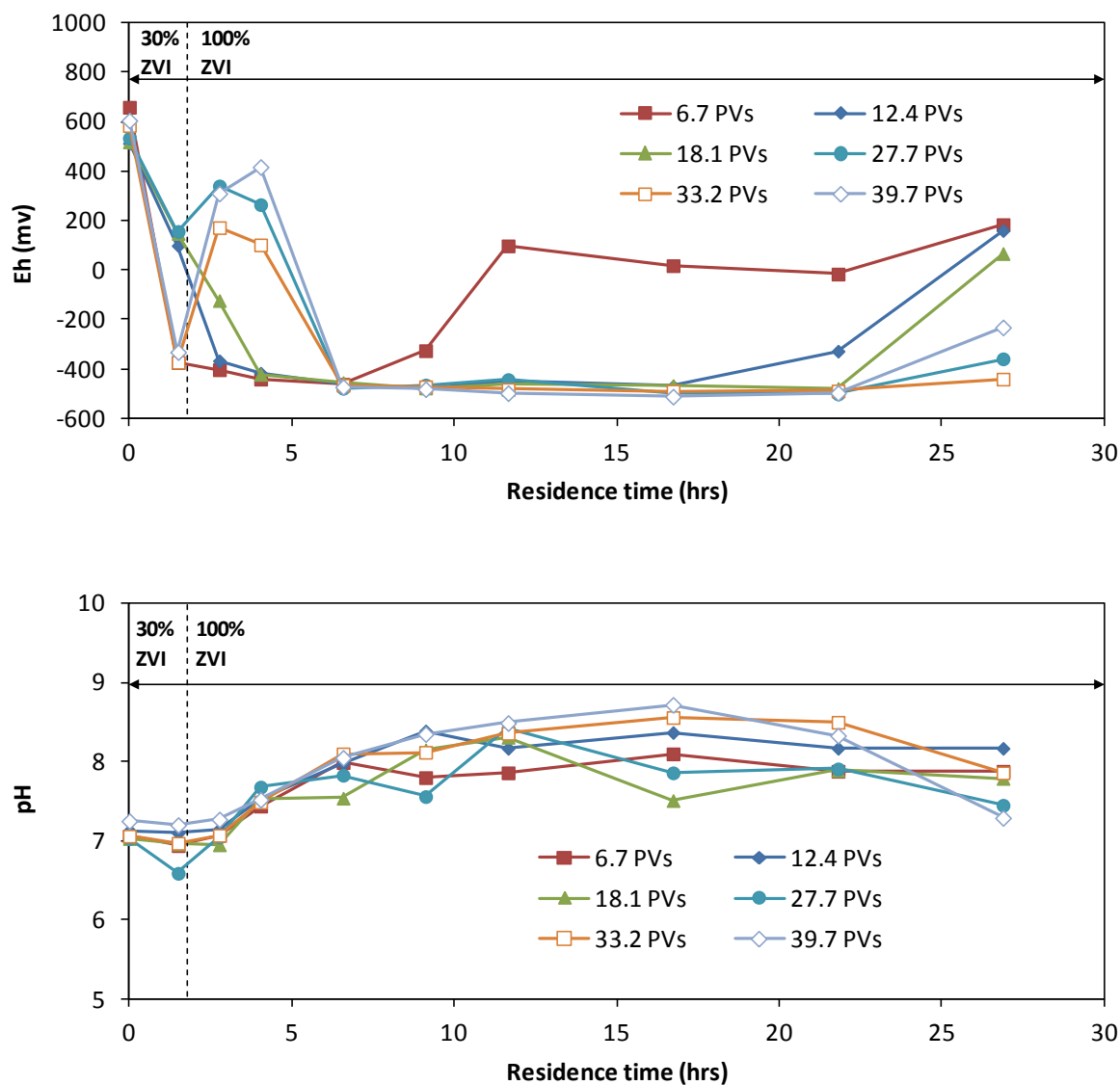


Figure 6: Redox potential (Eh) and pH profiles versus residence time in the column with increasing pore volumes (PVs) of water passed. Broken line indicates the extent of the 30% ZVI-70% sand zone vs. the main 100% ZVI zone. The 30%ZVI column was replaced after 28 PVs.

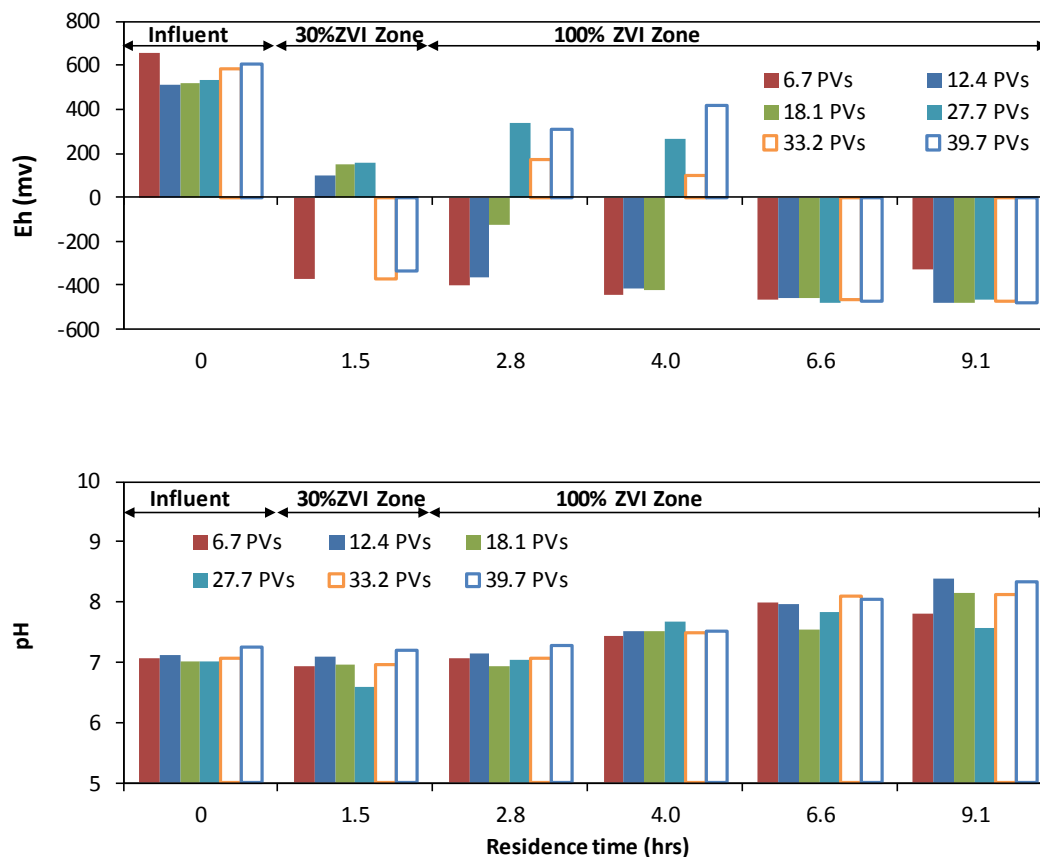


Figure 7: Eh and pH “breakthrough” in the influent part of the column system; including 5 cm long 30%ZVI-sand column and a 15 cm section of the 100% ZVI column. The 30%ZVI column was replaced after 28 PVs.

Appendix A

Laboratory Organic Analyses for Bench-Scale Testing Involving the ZVI Technology

Treatability Test
 ENVIRON 32421.10
 Dec-11

Column Identification: ETI#1074
 Column Composition: 100% Connelly CC1004
 Pore Volume (PV): 0.232 L
 Porosity: 0.623
 Column Length: 5 cm 30%ZVI-70%sand + 50 cm 100% ZVI
 Column Diameter: 1.5 in (3.8 cm)
 Flow Velocity: 1.6 ft/day (50 cm/day)
 Test Temperature: 22°C (72°F)

Column Distance (cm)	-5	0.0	2.5	5	10	15	20	30	40	50
Column Distance (ft)	-0.16	0.0	0.08	0.16	0.33	0.50	0.66	1.0	1.3	1.6
Residence Time (hr)	0	1.7	3.0	4.2	6.8	9.3	11.9	16.9	22.0	27.1

	PV	RN	30%ZVI	100%ZVI	Organic Concentration (µg/L)								Effluent	HL	r2
TCE	6.7	a	47	nd	nd	nd	nd	nd	nd	nd	nd	nd			
	12.4	a	68	nd	nd	nd	nd	nd	nd	nd	nd	nd			
	18.1	a	60	13	nd	nd	nd	nd	nd	nd	nd	nd			
	27.7	a	42	19	3.9	nd	nd	nd	nd	nd	nd	nd	0.54	0.996	
	33.2	b	47	8.9	nd	nd	nd	nd	nd	nd	nd	nd	0.25	1.000	
	39.7	b	46	11	3.6	nd	nd	nd	nd	nd	nd	nd	0.54	1.000	
cDCE	6.7	a	851	70	0.8	nd	nd	nd	nd	nd	nd	nd			
	12.4	a	784	176	1.3	nd	nd	nd	nd	nd	nd	nd			
	18.1	a	772	381	119	10	nd	nd	nd	nd	nd	nd			
	27.7	a	815	446	<u>326</u>	226	4.4	nd	nd	nd	nd	nd	1.4	0.923	
	33.2	b	717	280	<u>198</u>	153	6.3	nd	nd	nd	nd	nd	1.5	0.869	
	39.7	b	736	309	<u>223</u>	210	46	nd	nd	nd	nd	nd	1.9	0.844	
tDCE	6.7	a	30	2.0	2.0	2.0	2.1	2.1	1.7	1.3	1.1	1.1			
	12.4	a	25	3.3	2.2	1.3	1.5	1.9	2.0	1.5	1.6	1.2			
	18.1	a	22	7.1	2.9	1.8	1.6	1.3	1.7	1.6	0.8	0.9			
	27.7	a	16	7.4	3.8	2.6	nd	nd	nd	nd	nd	nd			
	33.2	b	21	6.1	3.7	2.7	nd	nd	nd	nd	nd	nd			
	39.7	b	20	5.1	3.3	2.7	nd	nd	nd	nd	nd	nd			
1,1-DCE	6.7	a	1.1	nd	nd	nd	nd	nd	nd	nd	nd	nd			
	12.4	a	1.3	nd	nd	nd	nd	nd	nd	nd	nd	nd			
	18.1	a	1.5	0.8	nd	nd	nd	nd	nd	nd	nd	nd			
	27.7	a	2.2	1.1	0.6	nd	nd	nd	nd	nd	nd	nd			
	33.2	b	1.3	nd	nd	nd	nd	nd	nd	nd	nd	nd			
	39.7	b	1.5	nd	nd	nd	nd	nd	nd	nd	nd	nd			
VC	6.7	a	96	6.6	nd	nd	nd	nd	nd	nd	nd	nd			
	12.4	a	83	14	nd	nd	nd	nd	nd	nd	nd	nd			
	18.1	a	70	30	8.7	1.6	nd	nd	nd	nd	nd	nd			
	27.7	a	52	28	<u>19</u>	14	1.0	nd	nd	nd	nd	nd	0.72	0.932	
	33.2	b	64	23	<u>15</u>	12	1.1	nd	nd	nd	nd	nd	0.95	0.901	
	39.7	b	65	21	<u>16</u>	15	4.5	nd	nd	nd	nd	nd	1.3	0.869	

PV = pore volume

RN = reservoir number

HL = half life (hours)

r2 = coefficient of determination

nd = not detected

Bold - Starting value for concentration profiles used in the fitting

Treatability Test
ENVIRON 32421.10
Dec-11

Column Identification: ETI#1074
Column Composition: 100% Connelly CC1004
Pore Volume (PV): 0.232 L
Porosity: 0.623
Column Length: 5 cm 30%ZVI-70%sand + 50 cm 100% ZVI
Column Diameter: 1.5 in (3.8 cm)
Flow Velocity: 1.6 ft/day (50 cm/day)
Test Temperature: 22oC (72oF)

Column Distance (cm)	-5	0.0	2.5	5	10	15	20	30	40	50
Column Distance (ft)	-0.16	0.0	0.08	0.16	0.33	0.50	0.66	1.0	1.3	1.6
Residence Time (hr)	0	1.7	3.0	4.2	6.8	9.3	11.9	16.9	22.0	27.1

	PV	RN	30%ZVI	100%ZVI	Organic Concentration (µg/L)							Effluent	HL	r2	
1,1,1TCA															
	6.7	a	311	nd	nd	nd	nd	nd	nd	nd	nd	nd			
	12.4	a	412	nd	nd	nd	nd	nd	nd	nd	nd	nd			
	18.1	a	395	24	nd	nd	nd	nd	nd	nd	nd	nd			
	27.7	a	346	43	10	nd	nd	nd	nd	nd	nd	nd	0.42	1.000	
	33.2	b	310	3.7	1	nd	nd	nd	nd	nd	nd	nd	0.63	1.000	
	39.7	b	324	4.0	nd	nd	nd	nd	nd	nd	nd	nd	0.63	1.000	
1,1DCA															
	7.7	a	nd	nd	nd	160	27	67	53	nd	nd	nd			
	13.2	a	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd			
	40.7	b	107	107	240	214	187	160	120	nd	nd	nd			
Nitrate (as N) mg/L															
	32.3	b	0.56	nd	nd	nd	nd	nd	nd	nd	nd	nd			
	38.8	b	0.52	nd	nd	nd	nd	nd	nd	nd	nd	nd			
Chloride (mg/L)															
	32.3	b	18	19	19	20	20	20	20	20	20	21			
	38.8	b	18	19	19	19	20	19	21	20	21	20			
Sulphate (mg/L)															
	32.3	b	260	270	250	240	240	240	240	250	270	260			
	38.8	b	260	260	240	230	230	220	220	230	240	250			
pH Values															
	6.7	a	7.1	6.9	7.1	7.4	8.0	7.8	7.9	8.1	7.9	7.9			
	12.4	a	7.1	7.1	7.2	7.5	8.0	8.4	8.2	8.4	8.2	8.2			
	18.1	a	7.0	7.0	7.0	7.5	7.5	8.2	8.3	7.5	7.9	7.8			
	27.7	a	7.0	6.6	7.1	7.7	7.8	7.6	8.4	7.9	7.9	7.5			
	33.2	b	7.1	7.0	7.1	7.5	8.1	8.1	8.4	8.6	8.5	7.9			
	39.7	b	7.3	7.2	7.3	7.5	8.1	8.4	8.5	8.7	8.3	7.3			
Eh (mV)															
	6.7	a	659	-374	-403	-441	-462	-326	98	18	-16	184			
	12.4	a	513	99	-367	-417	-461	-480	-450	-470	-328	160			
	18.1	a	519	148	-123	-422	-455	-477	-459	-467	-479	67			
	27.7	a	534	156	341	265	-478	-465	-443	-497	-501	-359			
	33.2	b	585	-373	172	102	-466	-472	-483	-490	-489	-441			
	39.7	b	605	-332	310	417	-473	-482	-498	-512	-497	-232			

PV = pore volume
RN = reservoir number
HL = half life (hours)
r2 = coefficient of determination
nd = not detected

Appendix B

Laboratory Inorganic Analyses for Bench-Scale Testing Involving the ZVI Technology

32421.10 Inorganics #1 results				
	Feed	Effluent	RDL	Units
Calculated Parameters				
Anion Sum	10.9	5.53	N/A	me/L
Bicarb. Alkalinity (calc. as CaCO ₃)	260	5.6	1.0	mg/L
Calculated TDS	631	362	1.0	mg/L
Carb. Alkalinity (calc. as CaCO ₃)	2.4	ND	1.0	mg/L
Cation Sum	11.0	6.12	N/A	me/L
Hardness (CaCO ₃)	500	260	1.0	mg/L
Ion Balance (% Difference)	0.580	5.10	N/A	%
Langelier Index (@ 20C)	1.05	-2.65	N/A	N/A
Langelier Index (@ 4C)	0.799	-2.90	N/A	N/A
Saturation pH (@ 20C)	6.95	9.02	N/A	N/A
Saturation pH (@ 4C)	7.20	9.27	N/A	N/A
Inorganics				
Ammonia-N	ND (1)	ND (1)	0.1	mg/L
Conductivity	1010	622	1	umho/cm
Organic Carbon	11.4	7.7	0.2	mg/L
Organic Carbon (TOC)	11	8.7	0.20	mg/L
Orthophosphate (P)	ND	ND	0.01	mg/L
pH	7.99	6.37	N/A	pH
Sulphate (SO ₄)	240	230	1	mg/L
Alkalinity (Total as CaCO ₃)	263	6	1	mg/L
Chloride (Cl)	19	21	1	mg/L
Nitrite (N)	ND	ND	0.01	mg/L
Nitrate (N)	0.5	ND	0.1	mg/L
Nitrate + Nitrite	0.5	ND	0.1	mg/L
Metals				
Aluminum (Al)	ND	ND	5	ug/L
Antimony (Sb)	1.1	1.2	0.5	ug/L
Arsenic (As)	ND	ND	1	ug/L
Barium (Ba)	49	78	2	ug/L
Beryllium (Be)	ND	ND	0.5	ug/L
Boron (B)	88	570	10	ug/L
Cadmium (Cd)	ND	ND	0.1	ug/L
Calcium (Ca)	130000	47000	200	ug/L
Chromium (Cr)	ND	ND	5	ug/L
Cobalt (Co)	ND	ND	0.5	ug/L
Copper (Cu)	2	ND	1	ug/L
Iron (Fe)	ND	ND	100	ug/L
Lead (Pb)	ND	ND	0.5	ug/L
Magnesium (Mg)	41000	34000	50	ug/L
Manganese (Mn)	ND	250	2	ug/L
Molybdenum (Mo)	4.4	4.3	0.5	ug/L
Nickel (Ni)	7	ND	1	ug/L
Phosphorus (P)	ND	ND	100	ug/L
Potassium (K)	3200	3400	200	ug/L
Selenium (Se)	ND	ND	2	ug/L
Silicon (Si)	5300	320	50	ug/L
Silver (Ag)	0.2	0.1	0.1	ug/L
Sodium (Na)	20000	21000	100	ug/L
Strontium (Sr)	380	100	1	ug/L
Thallium (Tl)	0.15	ND	0.05	ug/L
Titanium (Ti)	ND	ND	5	ug/L
Uranium (U)	7.8	ND	0.1	ug/L
Vanadium (V)	ND	ND	0.5	ug/L
Zinc (Zn)	ND	ND	5	ug/L
ND = Not detected				
N/A = Not Applicable				
RDL = Reportable Detection Limit				

32421.10 Inorganics #2 results				
	Feed	Effluent	RDL	Units
Calculated Parameters				
Anion Sum	10.3	5.59	N/A	me/L
Bicarb. Alkalinity (calc. as CaCO ₃)	239	4.8	1.0	mg/L
Calculated TDS	609	362	1.0	mg/L
Carb. Alkalinity (calc. as CaCO ₃)	2.2	ND	1.0	mg/L
Cation Sum	10.8	5.97	N/A	me/L
Hardness (CaCO ₃)	490	250	1.0	mg/L
Ion Balance (% Difference)	2.12	3.27	N/A	%
Langelier Index (@ 20C)	0.989	-2.57	N/A	N/A
Langelier Index (@ 4C)	0.741	-2.82	N/A	N/A
Saturation pH (@ 20C)	7.00	9.11	N/A	N/A
Saturation pH (@ 4C)	7.25	9.36	N/A	N/A
Inorganics				
Ammonia-N	ND (1)	ND (1)	0.1	mg/L
Conductivity	967	619	1	umho/cm
Organic Carbon	14.9	9.7	0.2	mg/L
Organic Carbon (TOC)	15	11	0.20	mg/L
Orthophosphate (P)	ND	ND	0.01	mg/L
pH	7.99	6.54	N/A	pH
Sulphate (SO ₄)	240	240	1	mg/L
Alkalinity (Total as CaCO ₃)	241	5	1	mg/L
Chloride (Cl)	19	21	1	mg/L
Nitrite (N)	ND	ND	0.01	mg/L
Nitrate (N)	0.5	ND	0.1	mg/L
Nitrate + Nitrite	0.5	ND	0.1	mg/L
Metals				
Aluminum (Al)	ND	ND	5	ug/L
Antimony (Sb)	ND	0.6	0.5	ug/L
Arsenic (As)	ND	ND	1	ug/L
Barium (Ba)	47	71	2	ug/L
Beryllium (Be)	ND	ND	0.5	ug/L
Boron (B)	82	520	10	ug/L
Cadmium (Cd)	ND	ND	0.1	ug/L
Calcium (Ca)	130000	44000	200	ug/L
Chromium (Cr)	ND	ND	5	ug/L
Cobalt (Co)	ND	ND	0.5	ug/L
Copper (Cu)	2	ND	1	ug/L
Iron (Fe)	ND	ND	100	ug/L
Lead (Pb)	ND	ND	0.5	ug/L
Magnesium (Mg)	42000	34000	50	ug/L
Manganese (Mn)	ND	250	2	ug/L
Molybdenum (Mo)	4.8	3.6	0.5	ug/L
Nickel (Ni)	6	ND	1	ug/L
Phosphorus (P)	ND	ND	100	ug/L
Potassium (K)	3300	3300	200	ug/L
Selenium (Se)	ND	ND	2	ug/L
Silicon (Si)	5400	140	50	ug/L
Silver (Ag)	ND	ND	0.1	ug/L
Sodium (Na)	21000	21000	100	ug/L
Strontium (Sr)	390	86	1	ug/L
Thallium (Tl)	0.14	ND	0.05	ug/L
Titanium (Ti)	ND	ND	5	ug/L
Uranium (U)	7.7	ND	0.1	ug/L
Vanadium (V)	ND	ND	0.5	ug/L
Zinc (Zn)	ND	ND	5	ug/L
ND = Not detected				
N/A = Not Applicable				
RDL = Reportable Detection Limit				

APPENDIX C

Methodology for Headspace SPME GC/ECD determination of VOCs in water samples SPME Protocol

Method developed by Michael Gibson, PhD.

Introduction:

Solid phase microextraction (SPME) followed by GC desorption and analysis has been demonstrated to be an effective and reliable method of monitoring volatile contaminants in water samples. SPME fibers can be desorbed in the manual injection ports of most gas chromatographs (GC), not requiring the specialized hardware necessary for purge and trap or headspace systems typically used for VOC analysis (Santos F.J. *et al.*, 1996).

The SPME fiber is a fused-silica fiber coated with a stationary phase, housed in a specialized syringe-type holder for protection and for inserting through septa. The fiber can either be immersed in an aqueous sample or be exposed to the headspace above an aqueous sample. The absorption of analytes is based on equilibrium partitioning between the coating and the sample. Where samples are contaminated with oils or other components which may damage or reduce the life of the fibers headspace analysis may be preferable. James and Stack (1997) compared headspace and immersion SPME for VOC analysis of wastewaters and found headspace SPME to be preferable.

The in-house method of analysis of VOCs in water samples was developed on the basis of headspace SPME followed by direct GC analysis.

Method:

The fibers used were Carboxen™/Polydimethylsiloxane with a 75µm thick stationary phase (Supelco No. 57318). Two (2) ml aqueous samples were placed in 4ml amber glass headspace vials with Teflon lined septa (Supelco No. 27006) with a 4 mm Teflon coated magnetic stir bar. Samples were stirred for 10 minutes prior to insertion of the fiber, the fiber was inserted (ensuring that it did not come in contact with the aqueous phase) for an additional 10 minutes. Fibers were removed from the samples and immediately (within 30 seconds) placed into the injection port of the GC for desorption and analysis.

Chromatographic analysis was performed using an Agilent 6890N series gas chromatograph coupled with a µECD detector. The injection port was lined with a small bore, 0.75 mm ID, glass liner (Supelco No. 26375-05). Both the injector and detector were maintained at 250 °C. Various split ratios, ranging from 25:1 to 250:1, were used depending on the analyte concentration. The analytical column was a VOCOL capillary column (30 m x 0.25 mm, 1.5 µm film thickness, Supelco No. 24205-U). Helium was used as the carrier gas; column flow rate was 0.5 ml/min. The column oven temperature program started at 40 °C for 2 min,

increased at 10 °C/min to 150 °C for 2 min, then increased at 30 °C to 200 °C for a final 2 min.

References.

James K J, Stack M A (1997) Fresenius J Anal Chem 358: 833-837.

Santos F J, Galceran M T, Fraisse D (1996) J. Chromatogr. A, 742: 181-189.